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# Symmetric Six-Fold Arrays of Photo- and Electrochromic Dithienylethene Switches

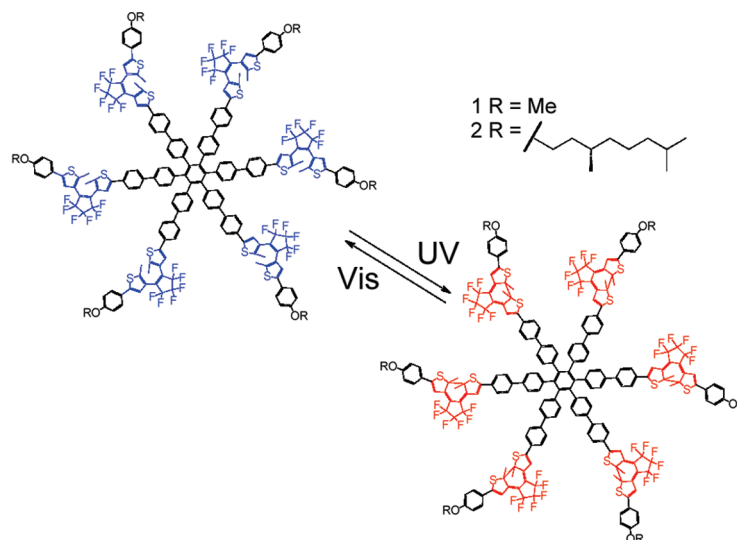
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## ABSTRACT



The direct synthesis of six-fold symmetric hexaphenylbenzenes with multiple photochromic dithienylethene units via a cobalt-catalyzed cyclotrimerization is reported. This approach allows for six photochromic units to be held in proximity with a well-defined spatial separation without affecting the photochromic properties of each unit.

The design and synthesis of highly symmetric (e.g., star-shaped) macromolecules such as hexaarylbenzenes are of current interest in material science owing to their potential for application in host–guest systems,<sup>1</sup> self-assembly,<sup>2</sup> energy storage in chromophore aggregates,<sup>3</sup> and liquid crystal technologies,<sup>4</sup> through the control they provide over the

orientation of functional units.<sup>5</sup> Hexaarylbenzenes, due to their symmetry and relative rigidity, are key structural components on which to assemble,<sup>6</sup> in a highly spatially controlled manner, redox and photoresponsive molecular units. Assemblies containing multiple redox- and photoactive

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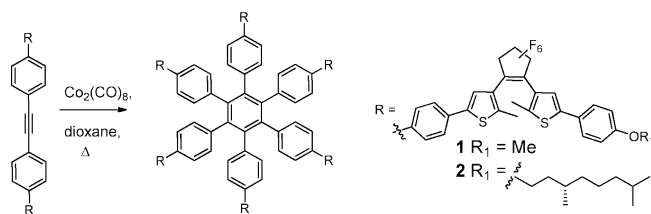
units require, in addition to a rigid scaffold, robust and synthetically accessible functional units.

Dithienylethenes show remarkable photo- and electrochromic behavior that can be tuned readily through synthetic modification. Importantly, they show often excellent photostationary states, reversibility of switching, and high fidelity between open (colorless) and closed (colored) forms upon irradiation with UV and visible light, respectively.<sup>7</sup> In addition, the dithienylethene unit shows bidirectional redox-driven switching both intrinsically<sup>8</sup> and through appended redox-active units.<sup>9</sup> The versatility of dithienylethene subunits as components for functional materials has been demonstrated already<sup>7</sup> and allows for reversible photochemical control of properties as diverse as fluorescence,<sup>10</sup> self-assembly,<sup>11</sup> and molecular conductivity.<sup>12</sup> In designing a multichromophoric array, an important consideration is interchromophore interactions and their effect on the efficiency of photo- and electrochemical switching.

Multicomponent molecular systems for multimode switching based on the dithienylethene photochromic unit have been reported recently where two or more switches are connected covalently via a single methylene,<sup>13</sup> ethynylene,<sup>14</sup> diyne,<sup>15</sup> phenylene,<sup>16</sup> or silyl<sup>17</sup> bridge. The photochemical properties of these multicomponent systems have proven to be sensitive to the nature of the bridging unit ranging from complete inhibition of double ring closing<sup>13–15</sup> to a complete absence of interaction and hence ring closure of all units.<sup>16,17</sup> A key challenge is therefore to achieve a high density of switching units in a controlled spatial arrangement without affecting the individual switching properties of the constituent units.

Here we report the synthesis, photo- and redox chemistry of star-shaped dithienylethene-substituted hexaphenylbenzenes **1** and **2** (Scheme 1), prepared via cobalt-catalyzed cyclotrimerization of alkynes, in which six (**1**, **2**) or one (**3**) photochromic units are connected around a central benzene core. Importantly the photo- and electrochemical behaviors

**Scheme 1.** Synthesis of **1** and **2**



of the dithienylethene photochromic units are unaffected when held in the six-fold symmetric molecular arrangement despite the individual switching units being in proximity.

Compound **3**, in which only one dithienylethene unit is attached to a hexaphenylbenzene core, was prepared by treatment<sup>18</sup> of dithienylethene **4** with *t*-BuLi at ambient temperature. This was followed by reaction with tri-*n*-butylborate to generate a boronic acid intermediate, which was reacted immediately with iodo-hexaphenylbenzene<sup>19</sup> **5** in the presence of a palladium catalyst to yield **3** (51%). A similar approach using a six-fold Suzuki coupling reaction with hexakis-bromo-hexaphenylbenzene and the boronic ester prepared from dithienylethene **4** (even with 12 equiv of the boronic acid) resulted in recovery of starting materials and a mixture of regioisomers. Cobalt-catalyzed cyclotrimerization,<sup>20</sup> a well-known method for the synthesis of hexaarylbenzenes with diverse substituents, typically proceeds in good yields, even where the substituents are dendrons with large molecular volumes.<sup>21</sup> In the present study, this route proved equally effective and provided direct access to hexaphenylbenzenes **1** and **2** in good yield (Scheme 1). Treatment<sup>18</sup> of dithienylethene **4** with *t*-BuLi and subsequent reaction with tri-*n*-butylborate generated a boronic acid intermediate, which was reacted with 4-bromo-4'-iodobiphenyl<sup>22</sup> in the presence of a palladium catalyst to yield compound **6** in 74% yield. The introduction of a branched alkyl chain was achieved by demethylation of compound **6** with boron tribromide, followed by ether formation using (*S*)-1-bromo-3,7-dimethyloctane, to yield dithienylethene monomer **7** in 57% overall isolated yield.

A Stille coupling reaction<sup>23</sup> was used instead in the synthesis of bis-dithienylethene acetylenes **8** and **9**. Bis-(tributylstannyl)acetylene served as the linker for 2 equiv of either **6** or **7**. The bis-dithienylethene acetylenes **8** and **9** were

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**Table 1.** Electronic Absorption and Redox Data for Open and PSS<sub>365nm</sub> (Closed) States

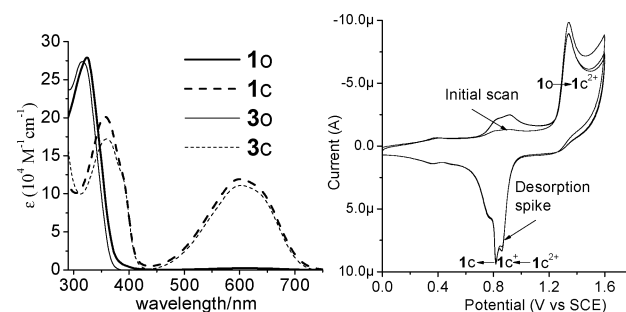
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	abs $\lambda_{\text{max}}/\text{nm}$ ( $\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) <sup>a</sup>	$E_{\text{p,a}}$ <sup>b</sup>	abs $\lambda_{\text{max}}/\text{nm}$ ( $\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) <sup>a</sup>	$E_{1/2}$ <sup>a</sup>	$E_{\text{p,c}}$ <sup>b</sup>
<b>1</b>	316 (50)	1.34(irr)	359 (31.5), 602 (20.1)	0.79, 0.86	−1.24 (irr), −1.61(irr)
<b>2</b>	324 (290)	1.29(irr)	357 (201.3), 602 (120.9)	0.78, 0.87	−1.33(irr), −1.85 (irr)
<b>3</b>	324 (304)	1.42(irr)	359 (222), 602 (131)	0.78, 0.92	−1.20(irr), −1.58(irr)
<b>6</b>	290 (65.6)	1.34(irr)	345 (31.0), 596 (17.3)	0.80, 0.93	n.d.
<b>7</b>	312 (51.9)	1.34(irr)	348 (35.3), 602 (21.4)	0.80, 0.93	n.d.
<b>8</b>	347 (106.1)	1.40(irr)	396 (89.5), 605 (48.3)	0.79, 0.90	n.d.
<b>9</b>	344 (102)	1.32(irr)	366 (91.0), 607(50.9)	0.79, 0.92	n.d.

<sup>a</sup> In toluene at 298 K. <sup>b</sup> With 0.3–1.1 mM in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M TBAPF<sub>6</sub> at 298 K; irr = irreversible.

prepared in 66 and 67% yield, respectively, by a double Stille-type<sup>24</sup> reaction. A cobalt-catalyzed<sup>25</sup> cyclotrimerization of bis-dithienylethene acetylenes **8** and **9** was carried out with catalytic Co<sub>2</sub>(CO)<sub>8</sub> heated at reflux in 1,4-dioxane under an argon atmosphere, affording compounds **1** and **2** in 44 and 66% yield, respectively. **1** and **2** were soluble in common organic solvents, such as dichloromethane, chloroform, and toluene, and were characterized by <sup>1</sup>H/<sup>13</sup>C NMR spectroscopy and MALDI-TOF mass spectrometry.<sup>18</sup> Formation of the hexaphenylbenzene core in **1** and **2** was confirmed by comparison with the <sup>13</sup>C NMR spectra of **8** and **9**.<sup>18</sup> In particular, the characteristic resonances corresponding to the sp-hybridized C atom at  $\delta = 90.2$  ppm for compounds **8** and **9** are not present for **1** and **2**, whereas an additional resonance around  $\delta = 136.8$  ppm is observed in the spectra of **1** and **2**. The signal is attributed to the six equivalent sp<sup>2</sup>-hybridized C atoms of the central phenyl cores of **1** and **2**, and the data are similar to those described for hexaarylbenzenes.<sup>26</sup> MALDI-TOF mass spectrometry showed molecular ions at  $m/z = 3824$  and  $4581$ , as expected for **1** and **2**, respectively.

UV–vis absorption data of **1–3** and **6–9** are summarized in Table 1. Irradiation of the open form with UV light (365 nm) results, in all cases, in formation of the closed form with a photostationary state (PSS) of >90% (vide infra). The switching behavior of compounds **1–3** is excellent, and photochromic switching can be performed over several cycles without degradation. Figure 1a shows the UV–vis absorption spectra of the open and closed form of the star-shaped dithienylethene-substituted hexaphenylbenzenes **1** and **2** in toluene. Upon irradiation of **1** and **2** at 365 nm, the colorless solution of the open forms turned blue, with the appearance of an absorption maximum at 602 nm. Importantly, the rates of ring closure for the hexa- (**1/2**) and monosubstituted (**3**) hexaphenylbenzenes are essentially identical, indicating that each switching unit behaves independently.<sup>18</sup> The absorption maxima of the closed forms of **1** and **2** are essentially the same as those of **3** and **6–9**, respectively.

The absence of a significant difference indicates that little or no interaction between chromophores is mediated by either



**Figure 1.** Left: UV–vis absorption spectra of open and PSS<sub>365nm</sub> of **1** and **3** (note that the molar absorptivity ( $\epsilon$ ) of **3** has been multiplied by 6 to allow for comparison of spectral shape) in toluene. Right: Cyclic voltammetry of **1o** at a glassy carbon working electrode in 0.1 M TBAPF<sub>6</sub>/CH<sub>2</sub>Cl<sub>2</sub> vs SCE at 0.1 V s<sup>−1</sup>.

the diphenylacetylene or hexaphenylbenzene cores. The absorption spectra of **1o** and **3o** are shown in Figure 1. Upon irradiation at 365 nm, both **3o** and **1o** undergo photocyclization, and two absorption bands appear in the visible region, corresponding to **1c** and **3c**, respectively, with the same maximum at 602 nm. The molar absorptivity of **1c** is 6 times that of **3c**, confirming that the PSS<sub>365nm</sub> (in terms of the total number of photochromic units) for **1** is essentially identical to **3**.<sup>27</sup>

FTIR spectroscopy has been shown previously to be a versatile method for nondestructive readout of the state of photochromic switches, not least dithienylethenes.<sup>28</sup> Since absorbance is linearly dependent on concentration, FTIR spectroscopy can be used to estimate the photostationary state achieved upon irradiation at  $\lambda_{365\text{nm}}$ . In Figure 2, FTIR ATR spectra are shown of a thin film of **2c** (i.e., at the PSS<sub>365nm</sub>). Upon irradiation at >400 nm, full conversion to the ring-opened state is observed. Subsequent irradiation of the ring-opened film at 365 nm leads to >90% conversion to the ring-closed state.

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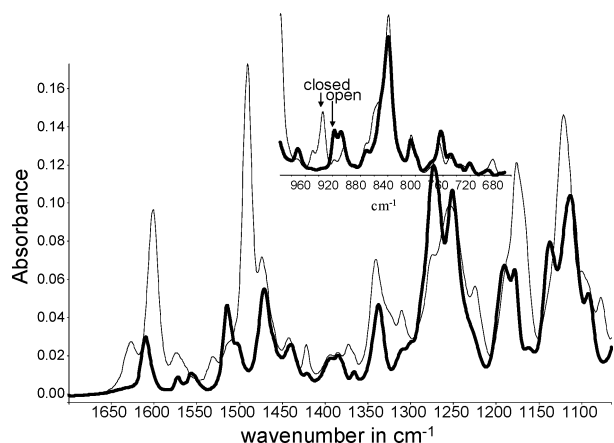
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**Figure 2.** FTIR spectra of **2o** (thick line) and at the PSS<sub>365nm</sub> (thin line); samples in CH<sub>2</sub>Cl<sub>2</sub> were deposited by evaporation onto a ZnSe/diamond ATR crystal. The band at 897 cm<sup>-1</sup> is present only in the open state and at 914 cm<sup>-1</sup> in the closed state.

The electrochemical properties of all compounds (Table 1) are in accordance with those of related dithienylethene switches reported previously.<sup>8</sup> In the open state, all compounds undergo an irreversible oxidation at 1.42 V (vs SCE), and on the return cycle, two new reversible redox processes at 0.78 and 0.92 V (vs SCE) are observed at potentials coincident with those of the closed forms. This indicates that oxidative ring closure to **3c**<sup>2+</sup>, for example, is occurring. Intermediate **3c**<sup>2+</sup> can then be reduced, first to **3c**<sup>+</sup> and finally to **3c**. In addition, two irreversible reduction steps are observed at -1.24 and -1.61 V (vs SCE) (not shown). The characteristic cyclic voltammetry together with the absence of a redox process between -2 and 1.5 V for the iodo-hexaphenylbenzene **10** supports the assignment that the oxidative processes observed are due to the dithienylethene units.

The hexadithienylethene-substituted **1** shows the characteristic irreversible oxidation at  $E_{p,a} = 1.34$  V (vs SCE), leading to oxidative ring closing to **1c**<sup>2+</sup> (Figure 1), which is subsequently reduced first to **1c**<sup>+</sup> and finally to **1c**. The cyclic voltammetry shows distinct differences with that of **3o** because the highly charged polycationic species formed upon oxidation is insoluble in CH<sub>2</sub>Cl<sub>2</sub> and deposits on the electrode surface. As a consequence, on the subsequent cathodic sweep, a desorption spike<sup>29</sup> at 0.83 V is observed, where the precipitated polycationic molecules are reduced to the more soluble **1c**<sup>6+</sup> and subsequently neutral **1c** state, allowing it to desorb from the surface of the electrode and return to solution. The adsorption and desorption of **1c**<sup>12+</sup>

were confirmed by resonance Raman spectroscopy.<sup>18</sup> Cyclic voltammetry of **2o**, which bears alkyl chains to increase solubility, shows electrochemical behavior similar to that of **3o**.

Overall, it is important to note that irrespective of the number of the redox-active dithienylethene groups (i.e., six dithienylethene units in **1** and **2**, two in compounds **8** and **9**, and one in the compound **3**) these dithienylethenes show essentially the same characteristic cyclic voltammetry, indicating that the dithienylethene units are not coupled electronically and are sufficiently well-separated to minimize electrostatic interactions.<sup>30</sup> Thus, the redox waves observed for **1c** and **2c** can be assigned to simultaneous multiple electron transfer<sup>31</sup> to produce highly charged stable species. Here we have described the synthesis and spectroscopic and electrochemical characterization of C<sub>6</sub>-symmetric star-shaped hexa(dithienylethene)-substituted hexaphenylbenzenes **1** and **2** prepared using a simple cobalt-catalyzed cyclotrimerization. The synthetic approach facilitates the synthesis of hexaphenylbenzene-centered multidithienylethene systems in which the dithienylethene units behave independently; that is, each unit can be switched photo- or electrochemically. Importantly, there is no indication of intramolecular interaction between the dithienylethene moieties, which is likely to be due to the twisted conformation of the hexaphenylbenzene core. The orientation of the phenyl rings in a paddle-wheel-type conformation is anticipated to be the origin of the absence of intercomponent communication and offers to be a versatile future scaffold for high-density arrangement of functional units. This approach to arranging chromophores is expected to be general and allow for straightforward synthetic access to systems in which multiple photochemical and redox-active units are arranged with a high degree of order and retention of molecular properties. Furthermore, the solubility of these systems allows for further modification at their periphery with additional functional units. This provides an additional advantage when constructing highly ordered functional arrays.

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**Supporting Information Available:** Synthesis and characterization of all compounds. NMR, FTIR, Raman and UV-vis absorption spectra, and electrochemical data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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